

# Fused Azulenes: Possible Organic Multiferroics

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We study low-lying correlated electronic states of fused azulenes using the long-range interacting Pariser-Parr-Pople model and the finite density matrix renormalization group method. The ground state is a singlet for oligomers with up to 5 azulene units. For oligomers with more than 5 azulene units and beyond 6 azulene units the oligomers have a triplet ground state. From the excitation gaps between the lowest  $M_S = 0$  state and the lowest states in  $M_S = 1, 2$  and 3 sector we predict that the ground state spin of the fused azulene increases with number of azulene units. In the thermodynamic limit we expect the fused azulene to be a ferromagnet. Charge density calculations show that the ground state of the system has ferroelectric alignment of the dipoles of the monomeric units. Thus, a fused azulene system could be the first example of a molecule which is both ferromagnetic and ferroelectric in the ground state.

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## INTRODUCTION

Conjugated organic materials have been attracting much attention for many electronic applications such as light emitting diodes[1, 2], photovoltaic cells(PVC)[3], and thin film transistors[4], to name a few. These materials are usually conjugated polymers such as MEH-PPV[5], PF2/6[6], PHT[7] which comprise of conjugated back bones built from phenyl or other ring systems. In recent years, fused systems such as oligo acenes have also come to the fore [8–11]. Pentacene has become important because its lowest triplet state has an excitation energy which is slightly less than half the singlet excitation gap, allowing multi exciton generation (MEG)[11] through singlet fission. If the open cell voltage in triplet dissociation is not small compared to singlet dissociation, the efficiency of the PVC can be significantly enhanced. This new paradigm has inspired a search for conjugated systems with low energy triplets.

One design principle that can lead to a low energy triplet state is incorporation of frustration in transfer topology of the molecule. The ground state as well as the lowest triplet state are dominated by covalent states (states with one electron per site). Their stabilization arises from delocalization of electrons in these states. In the singlet state the delocalization is reduced if the system is frustrated thereby increasing its energy. However, the triplet state in frustrated systems does not experience such enhanced frustration. This results in a reduction of the singlet-triplet gap.

A simple frustrated conjugated molecule that has been well studied is azulene with fused five and seven member rings. It also has a dipole moment  $\sim 1.0D$  attributed to the Hückel  $4n + 2$  rule[12]. Fused azulenes have long-

range frustration and could lead to low-lying triplets. Besides, the dipole moment of the azulene monomer can also align resulting in a molecular ferroelectric phase. With this in focus, we have carried out a detailed study of the low-lying excitations of fused azulene using finite density matrix renormalization group (DMRG) technique. In the next section, we briefly discuss the model Hamiltonian and the DMRG method used in our study. In the last section we present our results and discussions.

## MODEL HAMILTONIAN AND THE DMRG METHOD FOR FUSED AZULENES

The  $\pi$  system in fused polyazulenes (Fig. 1a) is modeled by considering one  $p_z$  orbital on each carbon atom. The Pariser-Parr-Pople (PPP) model[13, 14] Hamiltonian is given by,

$$H_{PPP} = \sum_{\langle ij \rangle} t(\hat{a}_{i,\sigma}^\dagger \hat{a}_{j,\sigma} + H.c.) + \frac{U}{2} \sum_i \hat{n}_i(\hat{n}_i - 1) + \sum_{i>j} V_{ij}(\hat{n}_i - 1)(\hat{n}_j - 1) \quad (1)$$

with the symbols having their usual meanings. The pentagons and the heptagons are treated as regular polygons of side 1.397 Å. The transfer integral between bonded sites is taken to be -2.4 eV. The Hubbard parameter  $U$  for Carbon is fixed at 11.26 eV. The inter-site interactions are parameterized using the Ohno[15] formula. The PPP model with these standard parameters have been extensively used for successfully modeling the excitations in a host of conjugated molecules.

The DMRG[16] method initially developed was a technique for studying correlated Hamiltonians such as the

Hubbard and Heisenberg models. In chemistry, the method has proved to be ideally suited to study conjugated polymeric system, within model Hamiltonian approaches. It has been shown that the DMRG method is accurate even in the presence of long-range interactions if these interactions are diagonal in real space, as with PPP model. This follows from comparing the DMRG results with exact diagonalization results for short chains as well as from entanglement entropy analysis of their exact eigenstates[17]. Many of the interesting conjugated polymers consist of ring systems, such as the phenyl, pyridine, thiophene, furan or pyrrole rings. Building the desired oligomer by adding two sites at each infinite DMRG step is nontrivial and the general method was first illustrated for the case of poly para phenylenes[18]. A similar approach can be used for building fused polyazulenes.

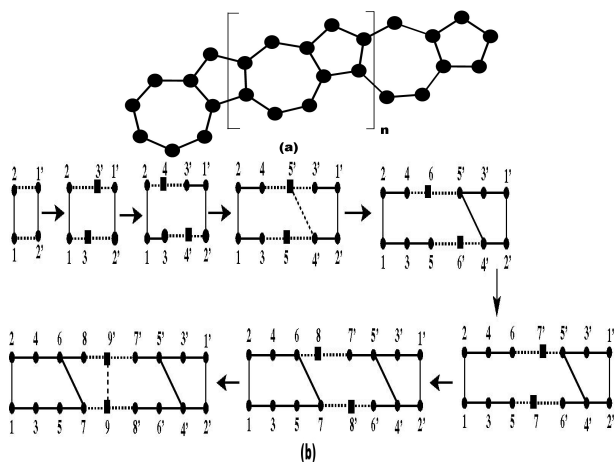


FIG. 1. (a) Structure of fused azulene, (b) DMRG scheme for building fused azulene.

The starting point in the infinite DMRG scheme is a four membered ring, at each iteration two sites are added in the middle of the ring and the ring size is expanded till we reach a ring size of ten at which point, an additional bond is introduced between the new site and a site added at the previous iteration, both being in the same block (Fig. 1 b ). The procedure is continued until we reach the oligomer of the desired size. After this point we start the finite DMRG sweeps in the usual manner[16].

We have checked our DMRG calculations against the noninteracting model results for all oligomers, for different cut-offs in the number of dominant density matrix eigenvectors,  $m$ . The ground state energy for a system of 3 fused azulenes agrees to almost 1ppm for  $m = 500$ . We have also checked the accuracy of our results for smaller system sizes and have found that the the ground and as the lowest excited state energies agree to better than  $4 \times 10^{-4} \text{ eV}$  for this cut-off. Hence in all our studies we have set  $m = 500$ .

## RESULTS AND DISCUSSION

Fused azulenes can have different structures, in one structure, the upper “polyene” chain is trans-trans while the lower “polyene” chain is cis-cis (Fig. 1a). In another structure, both the upper and lower “polyene” chains are cis-trans. We have carried out the DMRG calculations on the structure in Fig. 1a. Since the difference between the two structures arises only in third nearest neighbor, the electronic structure is not expected to be very different in the two cases. The energy per azulene unit linearly extrapolate to  $-19.117 \text{ eV}$  in the thermodynamic limit.

Spin gap in these oligomers is usually computed as the difference in energy between the lowest energy states in the  $M_s = 1$  sector and that in the  $M_s = 0$  sectors (the system has an even number of electrons). This is based on the assumption that the ground state is a singlet and the lowest spin excited state is a high spin state; the singlet state is found in the  $M_s = 0$  sector and states with nonzero spin are found in the  $M_s = 1$  sector. Furthermore, it is often assumed that the lowest energy spin state in the  $M_s = 1$  space is a triplet. Accordingly, we computed the lowest energy states in the  $M_s = 0$  and  $M_s = 1$  subspaces. Our studies showed that for oligomers with more than five azulene units the lowest energy states in these two subspaces were degenerate within the accuracy of the calculation. This implies that the ground state has a spin  $S \geq 1$ .

To determine the spin of the ground state in the longer oligomers ( $n \geq 6$ ), we computed two lowest energy states in the  $M_s = 0$  and  $M_s = 1$  subspaces and the lowest energy state in the  $M_s = 2, 3$  subspace. In these oligomers, the lowest energy state in  $M_s = 2$  state is higher in energy than the degenerate lowest energy states in the  $M_s = 0$  and 1 subspaces. This conclusively proves that the ground state in these oligomers is a triplet. To investigate whether in even longer fused azulenes, the ground state again switches from  $S = 1$  to higher spin, we investigated the gaps between the lowest energy  $M_s = 0$  state and lowest energy states in  $M_s = 1, 2$  and 3, as function of the number of oligomers (Fig. 2). We note that the slopes for these different gaps in Fig. 2 are different and it appears that as the system size increases, the ground state will switch initially from  $S = 0$  to  $S = 1$  as seen from the vanishing of the gap between the lowest energy levels in the  $M_s = 1$  and  $M_s = 0$  sector. From the behavior of the gap between the lowest  $M_s = 2$  and  $M_s = 0$  level, we see that these gap is also going to vanish when the system size increases to about 10 or 11 azulene units leading to spin  $S = 2$  ground state. The gap  $\Delta_3$  between lowest  $M_s = 3$  and  $M_s = 0$  levels also appears to vanish for even larger systems, making  $S = 3$  ground state. Therefore, it is likely that in the polymer limit, a ferromagnetic ground state will result. Polymers with triplet ground state are, to the best of our knowledge not

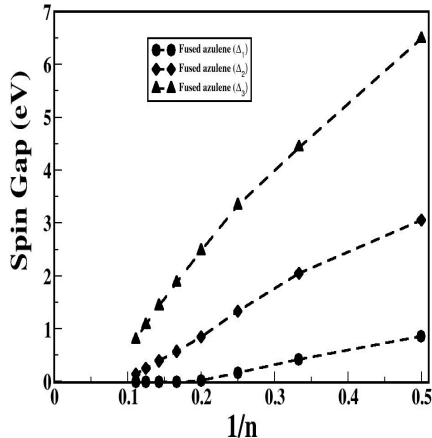


FIG. 2. Spin gaps (in eV) vs  $\frac{1}{n}$ . ( $\Delta_1 = (E_{M_S=1} - E_{M_S=0})$ ,  $\Delta_2 = (E_{M_S=2} - E_{M_S=0})$ , and  $\Delta_3 = (E_{M_S=3} - E_{M_S=0})$ ). These states correspond to the lowest energy state in their respective  $M_s$  sector.

known, although Monkman and coworkers[19], based on the correlation between experimental singlet and triplet excitation energies, predicted that a polymer will have a triplet ground state, if the singlet exciton energy is below 1.3 eV. However, there is no theoretical basis for this prediction and is just based on extrapolation of the plot of singlet exciton energy vs triplet exciton energy from experiments, for various polymers. To see if the system is a polymeric example of flat-band ferromagnetism, we examined the non-interacting one-particle states of the system with 12 azulene units. We find that there is no degeneracy of the nonbonding molecular orbitals(MOs) at  $E_F$ , which is a requisite for flat band ferromagnetism[20]. These results show that for fused azulene with less than six azulene units, the MEG process can create multiple triplet excitations. However, it is not clear whether it will lead to higher efficiencies in a PVC as the voltage obtained for the cell could be quite low, due to small triplet gaps.

To understand whether the high spin ground state results from isolated azulene units in the polymer or is a specific property associated with fused systems, we have also carried out DMRG studies on polyazulene which has two azulenes per unit cell and has successive azulene units connected by a  $C - C$  bond between pentagons. We have studied the spin gap in these systems by using finite DMRG algorithm with a cut-off in  $m$  of 400. For all sizes we have studied, we find that singlet is the ground state. The energy gap to the triplet state lies in the range  $1.08 \pm 0.04$  eV for the oligomers with 4, 6 and 8 azulene units. Thus, for observing a high spin ground state, it appears that the azulenes have to be

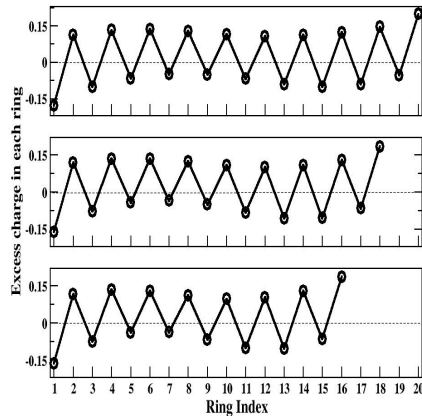


FIG. 3. Ring charges in fused azulenes with 8, 9 and 10 azulene units. Charge in a ring is given by  $(n - p)$ ,  $p$  = number of carbon atoms in the ring. Odd(Even) ring index corresponds to seven(five) membered ring of the azulene.

fused so that the bond frustration extends over the entire system. The polyazulene system has only localized bond-frustration, hence the singlet ground state is preferred. Bond-order of a bond  $(i, j)$  in the ground state is defined as  $\frac{1}{2} < \sum_{\sigma} \{a_{i,\sigma}^{\dagger} a_{j,\sigma} + a_{j,\sigma}^{\dagger} a_{i,\sigma}\} >$  and expectation value is the ground state expectation value. Bonds with large(small) bond orders will have a tendency to become shorter(longer) in the equilibrium geometry and thus indicate the equilibrium bond lengths when the system is allowed to relax its geometry. We note that in both the singlet and the triplet states, the bond orders for the peripheral bonds are nearly uniform. This shows that the system is unlikely to undergo a structural distortion.

This observation is important, since it is well known that low-dimensional systems can undergo a distortion of the Peierls' type which could lead to stabilization of the singlet state relative to the triplet state. We also note that the bond orders for the bonds that connect the upper and lower polyene like chains is rather small, implying that any distortion of the system will only uniformly increase the distance between the upper and lower chains, which is unlikely to alter energy level ordering of the low-lying states.

We have investigated the charge distribution in the oligomers. We have shown the net charge (equals sum of actual charges on the sites comprising the ring minus the number of sites in the ring) in the seven and five membered rings in the oligomers in Fig. 3. In all the oligomers studied, seven membered rings have positive charge while five membered ring have negative charge. The amplitude of the charge density wave in the system remains approximately the same, independent of the oligomer size and

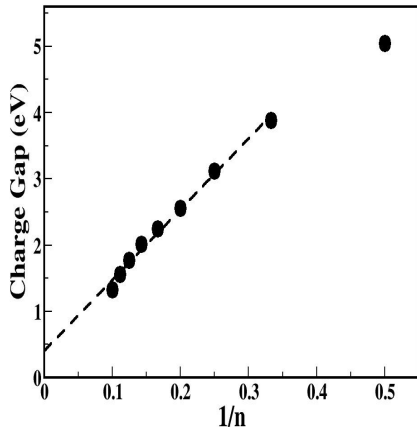


FIG. 4. Charge gap (in eV) vs  $\frac{1}{n}$ .

we expect a ferroelectric state in the polymer limit. This would mean that the fused azulene system in the thermodynamic limit, would be a multiferroic, showing both a ferromagnetic and a ferroelectric ground state.

Charge gap measures the energy required to create an independent electron-hole pair in a system. The charge gap for a polymeric system can be obtained by extrapolating  $E_c(N) = E^+(N) + E^-(N) - 2E_{gs}^0(N)$  (where  $N$  is the number of monomers and superscripts '+' and '-' refer to cation and anion while '0' refers to the neutral species) to the thermodynamic limit. The quantity  $E_c(N)$  gives the energy required to create a pair of free moving electron and hole in the ground state. The plot of charge gap vs  $\frac{1}{n}$  is shown in Fig. 4. Extrapolating the charge gap to thermodynamic limit, we obtain the value  $E_c(\infty) = 0.403$  eV. This is smaller than typical charge gaps found for conjugated polymers by almost an order of magnitude[21].

To conclude, we have studied low-lying electronic states in fused azulenenes using PPP model and finite DMRG scheme. We note that for short oligomers ( $< 6$  azulene units) the ground state is a singlet and the ground state switches to triplet for all the fused systems between 6 and 10 azulene units long. In the thermodynamic limit, we expect the chain to be ferromagnetic. This implies that MEG process could be important only in short fused azulene systems where the triplet is a low energy excited state. Bond order studies show that the bond along the upper and lower chain will remain uniform while it is likely that the separation between the upper and lower chains of fused azulene will increase in thermodynamic limit. The system also exhibits order-

ing of dipoles of the azulenenes with seven membered rings being positively charged and five membered rings negatively charged. This implies that the ground state will be both a ferromagnet and ferroelectric in the thermodynamic limit. Such a system would be the first example of a molecular multiferroics. The charge gap in these system is quite small compared to other polymers. These features of fused azulene should be of importance in organic device applications.

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